

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions, and listings, of claims in the application:

LISTING OF CLAIMS:

1-22. (Canceled)

23. (Currently Amended) A process for the preparation of first generation random microgels comprising a step of controlled radical polymerization of a composition comprising at least one monoethylenically unsaturated monomer, at least one polyethylenically unsaturated monomer, a source of free radicals, and a control agent,

wherein said first generation random microgels comprise a polymer having chain ends which can be activated by reversible transfer or by termination, said polymer comprising one or more thiocarbonylthio groups.

24. (Previously Presented) The process as claimed in claim 23, wherein the monoethylenically unsaturated monomer is:
styrene derivatives,
carboxylic acid vinyl esters,
vinyl halides, vinylidene halides,

unsaturated ethylenic monocarboxylic acids, unsaturated ethylenic dicarboxylic acids, the monoalkyl esters thereof with alkanols having 1 to 4 carbon atoms, optionally N-substituted,

amides of unsaturated carboxylic acids,

ethylenic monomers having a sulfonic acid group, an alkali metal or ammonium salts thereof,

amides of vinylamine,

unsaturated ethylenic monomers having a secondary, tertiary or quaternary amino group or a heterocyclic group having nitrogen, aminoalkyl (meth)acrylates, aminoalkyl(meth)acrylamides, zwitterionic monomers,

(meth)acrylic esters,

vinyl nitriles,

monomers having at least one boronate functional group or a precursor thereof,

phosphonates monomers comprising, N-methacrylamidomethylphosphonic acid ester derivatives,

phosphate monomers, monomers having a —C—O—P— sequence in comparison with the —C—P— sequence of the phosphonates, and

monomers carrying an alkoxy silane group selected from the group consisting of trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilyl-propyl methacrylate,

trimethoxysilylpropyl methacrylate, triethoxysilylpropyl meth-acrylate, tributoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate and tributoxysilylpropyl acrylate.

25. (Previously Presented) The process as claimed in claim 24, wherein the monoethylenically unsaturated monomer is:

α -methylstyrene, vinyltoluene, vinyl acetate, vinyl neodecanoate, vinyl propionate, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-alkylacrylamides, vinylsulfonic acid, vinylbenzenesulfonic acid, α -acrylamidomethylpropanesulfonic acid, 2-sulfoethylene methacrylate, vinylformamide, vinylacetamide, N-vinylpyrrolidone, N-vinylcaprolactam, vinylpyridine, vinylimidazole, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, di(tert-butyl)aminoethyl acrylate, di(tert-butyl)aminoethyl methacrylate, dimethylaminomethylacrylamide, dimethylaminomethylmethacrylamide, sulfopropyl(dimethyl)aminopropyl acrylate,

glycidyl acrylate, glycidyl methacrylate,

vinyl nitriles,

acryloylbenzeneboronic acid, methacryloylbenzeneboronic acid, 4-vinylbenzene-

boronic acid, 3-acrylamidophenylboronic acid,

3-methacrylamidophenylboronic acid, alone or as mixtures, or in the form of

salts,

n-propyl ester of N-methacrylamidomethylphosphonic acid, methyl ester of

N-methacrylamidomethylphosphonic acid, ethyl ester of

N-methacrylamidomethylphosphonic acid, n-butyl ester of

N-methacrylamidomethylphosphonic acid, isopropyl ester of

N-methacrylamidomethylphosphonic acid,

N-methacrylamidomethylphosphonic diacid; N-methacrylamidoethylphosphonic acid

dimethyl ester, N-methacrylamido-ethylphosphonic acid di(2-butyl-3,3-

dimethyl) ester, N-methacrylamidoethylphosphonic diacid,

N-acrylamidomethylphosphonic acid dimethyl ester,

N-acrylamidomethylphosphonic acid diethyl ester, bis(2-chloropropyl)

N-acrylamidomethylphosphonate, (N-acrylamidomethylphosphonic acid,

di(n-propyl) vinylbenzylphosphonate dialkyl ester, di(isopropyl)

vinylbenzylphosphonate dialkyl ester, diethyl vinylbenzylphosphonate dialkyl

ester, dimethyl vinylbenzylphosphonate dialkyl ester, di(2-butyl-3,3-dimethyl)

vinylbenzylphosphonate dialkyl ester, di(t-butyl) vinylbenzylphosphonate

dialkyl ester, vinylbenzylphosphonic diacid, diethyl 2-(4-vinylphenyl)

ethanephosphonate, 2-(acryloyloxy)ethylphosphonic acid dimethyl ester,

2-(methacryloyloxy)ethylphosphonic acid dimethyl ester,

2-(methacryloyloxy)methyl-phosphonic acid diethyl ester,
2-(methacryloyloxy)methylphosphonic acid dimethyl ester,
2-(methacryloyloxy)propylphosphonic acid dimethyl ester,
2-(acryloyloxy)methylphosphonic acid diisopropyl ester,
2-(acryloyloxy)ethylphosphonic acid diethyl ester,
2-(methacryloyloxy)ethylphosphonic acid,
2-(methacryloyloxy)methylphosphonic acid,
2-(methacryloyloxy)propylphosphonic acid,
2-(acryloyloxy)propylphosphonic acid, 2-(acryloyloxy)ethylphosphonic acid;
vinylphosphonic acid, optionally substituted by cyano, phenyl, ester or acetate
groups, vinylidenephosphonic acid the sodium salt thereof, the isopropyl ester
thereof, or bis(2-chloroethyl)vinylphosphonate.

26. (Previously Presented) The process as claimed in claim 24, wherein the monoethylenically unsaturated monomer is a styrene monomer, vinyl ester, neutral or charged hydrophilic acrylate, hydrophobic acrylate, neutral or charged hydrophilic methacrylate, hydrophobic methacrylate, hydrophilic or hydrophobic acrylamido derivatives, neutral or charged acrylamido derivatives, hydrophilic or hydrophobic methacrylamido derivatives, or neutral or charged methacrylamido derivatives.

27. (Previously Presented) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer is an organic compound reactive by the radical route comprising at least two ethylenic unsaturations and at most 10 ethylenic unsaturations.

28. (Previously Presented) The process as claimed in claim 27, wherein the polyethylenically unsaturated monomer is an acrylic, methacrylic, acrylamido, methacrylamido, vinyl ester, vinyl ether, diene, styrene, .alpha.-methylstyrene or allyl derivative.

29. (Previously Presented) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer further bears one or more functional groups other than ethylenic unsaturations selected from the group consisting of hydroxyl, carboxyl, ester, amide, amino, substituted amino, mercapto, silane, epoxy and halo functional groups.

30. (Previously Presented) The process of claim 23, wherein the polyethylenically unsaturated monomer is selected from the group consisting of divinylbenzene, vinyl methacrylate, methacrylic acid anhydride, allyl methacrylate, ethylene glycol dimethacrylate, phenylene dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol 200 dimethacrylate, polyethylene glycol 400 dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,12-dodecanediol dimethacrylate, 1,3-glycerol dimethacrylate, diurethane dimethacrylate or trimethylolpropane trimethacrylate; vinyl acrylate, bisphenol A epoxy diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polyethylene glycol 600 diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl

glycol ethoxylate diacrylate, butanediol diacrylate, hexanediol diacrylate, aliphatic urethane diacrylate, trimethylolpropane triacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, glycerol propoxylate triacrylate, aliphatic urethane triacrylate, trimethylolpropane tetraacrylate or dipentaerythritol pentaacrylate; vinyl crotonate, diethylene glycol divinyl ether, 1,4-butanediol divinyl ether or triethylene glycol divinyl ether; diallyl phthalate, diallyldimethylammonium chloride, diallyl maleate, sodium diallyloxyacetate, diallylphenylphosphine, diallyl pyrocarbonate, diallyl succinate, N,N'-diallyltartardiamide, N,N-diallyl-2,2,2-trifluoroacetamide, the allyl ester of diallyloxyacetic acid, 1,3-diallylurea, triallylamine, triallyl trimesate, triallyl cyanurate, triallyl trimellitate or 1,3,5-triallyltriazine-2,4,6(1H,3H,5H)-trione; N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, glyoxalbisacrylamide or diacrylamidoacetic acid; divinylbenzene and 1,3-diisopropenylbenzene; butadiene, chloroprene or isoprene.

31. (Previously Presented) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomer is N,N'-methylenebisacrylamide, divinylbenzene, ethylene glycol diacrylate or trimethylolpropane triacrylate.

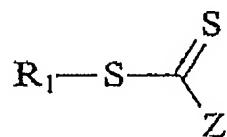
32. (Previously Presented) The process as claimed in claim 23, wherein the polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers are in a molar fraction of between 0.001 and 1.

33. (Previously Presented) The process as claimed in claim 32, wherein the molar fraction of polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers is between 0.01 and 1.

34. (Previously Presented) The process as claimed in claim 23, wherein the controlled radical polymerization is carried out according to a Atom Transfer Radical Polymerization (ATRP) process or by a reversible transfer by addition-fragmentation of thiocarbonylthio compounds process.

35. (Previously Presented) The process as claimed in claim 34, wherein the controlled radical polymerization is carried out according to a reversible transfer by addition-fragmentation of thiocarbonylthio compounds process.

36. (Previously Presented) The process as claimed in claim 35, wherein the thiocarbonylthio compounds are compounds of following formula (A):



(A)

wherein:

Z represents:

- a hydrogen atom,
- a chlorine atom,
- an optionally substituted alkyl radical or an optionally substituted aryl radical,

an optionally substituted heterocycle,
an optionally substituted alkylthio radical,
an optionally substituted arylthio radical,
an optionally substituted alkoxy radical,
an optionally substituted aryloxy radical,
an optionally substituted amino radical,
an optionally substituted hydrazine radical,
an optionally substituted alkoxycarbonyl radical,
an optionally substituted aryloxycarbonyl radical,
a carboxyl or optionally substituted acyloxy radical,
an optionally substituted aroyloxy radical,
an optionally substituted carbamoyl radical,
a cyano radical,
a dialkyl- or diaryl-phosphonato radical,
a dialkyl-phosphinato or diaryl-phosphinato radical,
or a polymer chain, and

R₁ represents:

an optionally substituted alkyl, acyl, aryl, aralkyl, alkenyl or alkynyl group, an
optionally substituted, aromatic, saturated or unsaturated, carbon ring or
heterocycle, or a polymer chain.

37. (Previously Presented) The process as claimed in claim 34, wherein the thiocarbonylthio compounds are xanthate, dithiocarbamate or dithioester compounds carrying a single functional group of formula —S(C=S)—.

38. (Previously Presented) The process as claimed in claim 37, wherein the compounds are xanthates.

39. (Currently Amended) A process for the preparation of second-generation random microgels, comprising the steps of:

- 1) preparing a first-generation random microgel wherein said preparation comprises a step of controlled radical polymerization of a composition comprising at least one monoethylenically unsaturated monomer, at least one polyethylenically unsaturated monomer, a source of free radicals, and a control agent, and
- 2) adding at least one mono- or polyethylenically unsaturated monomer to the microgel obtained in step 1) in the presence of an activator; wherein said first generation random microgels comprise a polymer having chain ends which can be activated by reversible transfer or by termination, said polymer comprising one or more thiocarbonylthio groups and said second generation random microgels comprise a core of a first generation random microgel and polymer arms extending from the chain ends which can be activated by the central portion.

40. (Previously Presented) A process for the preparation of nth-generation random microgels, n being an integer between 3 and 50, comprising the steps of:

- a) preparing a first-generation random microgel, wherein said preparation comprises a step of controlled radical polymerization of a composition

comprising at least one monoethylenically unsaturated monomer, at least one polyethylenically unsaturated monomer, a source of free radicals, and a control agent,

- b) preparing an 2nd generation random microgel by adding, in the presence of an activator, at least one mono- or polyethylenically unsaturated monomer to the first-generation microgel obtained in step a) in the presence of an activator to form a 2nd generation random microgel;
- c) preparing a next generation random microgel by adding in the presence of an activator at least one mono- or polyethylenically unsaturated monomer to the previous generation random microgel, where the step is performed n-2 times to form and (n-1)th generation random microgel; and
- d) preparing an nth generation random microgel by adding in the presence of an activator at least one mono- or polyethylenically unsaturated monomer to the (n-1)th generation random microgel obtained at the end of step c) in the presence of an activator.

41. (Previously Presented) The process as claimed in claim 39, wherein the activator is a source of free radicals.

42. (Previously Presented) The process as claimed in claim 39, wherein the monomer(s) used in step 2 is or are (a) monoethylenically unsaturated monomer(s) in order to obtain a star-shaped polymer.

43. (Previously Presented) The process as claimed in claim 40, wherein the monomer(s) used in step n is or are (a) monoethylenically unsaturated monomer(s) in order to obtain a star-shaped polymer.

44. (Previously Presented) The process as claimed in claim 43, wherein the star-shaped polymer exhibits (1) a central portion in the form of a first-generation microgel based on a crosslinked polymer resulting from the polymerization of the mono- and polyethylenically unsaturated monomers and (2) arms composed of the monoethylenically unsaturated monomers only added starting from step 2 and comprising, at their end, an active part of the control agent ($-\text{S}(\text{C}=\text{S})-$ functional group), in the case of a controlled radical polymerization process of reversible transfer by addition-fragmentation of thiocarbonylthio compounds type, or the halogen or pseudohalogen part, in the case of a controlled radical polymerization ATRP process.

45. (Previously Presented) The process as claimed in claim 44, wherein the active part of the control agent ($-\text{S}(\text{C}=\text{S})-$ functional group) is substituted in all or part by a hydrogen atom or a thiol functional group.